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AMORPHOUS SEMICONDUCTORS

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Prepared for:

Advanced Research Projects Agency
Army Research Office

31 March 1973

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Semiannual Technical Report
1 October 1972 -- 31 March 1973

AD 759849

ARPA Order Number 1562	Grant Number DA-ARO-D-31-124-72-C75
Program Code Number 0D10	James C. Thompson 512/471-5926
University of Texas at Austin--Grantee	James C. Thompson 512/471-5926
Effective Date: 1 April 1972	Amorphous Semiconductors
Expiration Date: 31 March 1973	
Amount of Grant: \$32,746.00	

Sponsored by

Advanced Research Projects Agency
ARPA Order No. 1562



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SUMMARY

We have continued and expanded direct measurements of the isothermal compressibility and acoustic determinations of the glass transition. The latter procedure has been tested extensively on two organic glasses so that comparison with previously existing data can be made. The installation of the laboratory in the new building is complete and welcome.

The work during the past six months is described in the following two sections which are based on papers which are ready for submission. The paper on acoustic determination of the glass transition will be sent to the Review of Scientific Instruments, and the paper on compressibility will be sent to the Journal of Non-Crystalline Solids.

Direct Measurement of Isothermal Compressibility of Amorphous Semiconductors*

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The isothermal compressibilities of the chalcogenide glasses $\text{Te}_{15}\text{Ge}_3\text{As}_2$, $\text{Te}_{15}\text{Ge}_2\text{As}_3$, and As_2Se_3 have been measured to 5 kbar by direct measurement of the change in sample length using a differential transformer placed inside the hydrostatic pressure vessel. Calibration data was obtained from the measurement of the compressibilities of alkali halide single crystals. For $\text{Te}_{15}\text{Ge}_3\text{As}_2$, the isothermal compressibility was found to be $6.23 \times 10^{-12} - 1.6 P \times 10^{-22} \text{ cm}^2/\text{dyne}$; for $\text{Te}_{15}\text{Ge}_2\text{As}_3$, $5.86 \times 10^{-12} - 0.5 P \times 10^{-22} \text{ cm}^2/\text{dyne}$; for As_2Se_3 , $6.43 \times 10^{-12} - 1.0 P \times 10^{-22} \text{ cm}^2/\text{dyne}$ where P is the pressure in dynes/cm². Errors are near 5%.

*This research was supported in part by the Advanced Projects Agency of the Department of Defense and was monitored by U. S. Army Research Office-Durnam under Grant No. DA-ARO-D-31-124-73-G81.

1. INTRODUCTION

There has been considerable recent interest in the electronic properties of amorphous semiconductors. We have directed our attention toward the mechanical properties of these materials, specifically at high pressure. As one facet of this investigation, the isothermal compressibilities of $\text{Te}_{15}\text{Ge}_3\text{As}_2$, $\text{Te}_{15}\text{Ge}_2\text{As}_3$, and As_2Se_3 have been measured to 5 kbar.

Since glass is an isotropic solid, it is sufficient to measure the change in length of the solid under pressure to calculate the compressibility. There are a variety of techniques. Bridgman, in the majority of his measurements at lower pressures, used a linear potentiometer technique¹). Strain gauge techniques have also been used²). Recently differential transformer techniques³⁻⁸) have been used to measure linear dilation because the instrumentation is somewhat less complicated.

2. EXPERIMENTAL PROCEDURE

A linear variable differential transformer⁹) (LVDT) was used to measure the change in length of the glass under hydrostatic pressure. The LVDT and sample holder, as shown in Fig. 1, were placed inside a 10 kbar pressure apparatus of the Bridgman design using nitrogen gas as the pressure medium. The spring-loaded copper plunger directly followed the relative change in length of the sample as compared to the iron sample holder. The plunger was connected to the magnetic core of the LVDT. As the sample length decreased, relative to the linear compression of the sample holder, the LVDT core moved and the output from the LVDT was changed. The screw section at the bottom of the sample holder allowed different size samples to be measured. With the exception of the NaCl calibration sample, the samples used in this investigation were 2 cm long. The spring at the top of the sample holder held the LVDT in place.

Primary excitation of the LVDT at 2.5 kHz and amplification and detection of the output was provided by a standard Schaevitz Engineering Model No. CAS 2500 signal conditioner. The output from the signal conditioner and from the manganin pressure gauge were simultaneously displayed on an x-y recorder.

The chalcogenide glasses were prepared by weighing out the component elements into a quartz ampule. The quartz ampule was evacuated and sealed. The sample was held at 800°C (600°C in the case of As_2Se_3) in a rocking furnace for 24-48 hours before being quenched. The glasses were not annealed.

3. RESULTS

The apparatus was calibrated by measuring the linear dilation of NaCl, KCl, KBr, and KI single crystals obtained from Harshaw Chemical Co. The change in length under pressure (Δl), as well as the length at atmospheric pressure (l_0), were measured for the alkali halide single crystals and for the glasses at room temperature of 23°C. Some of the measured quantities are shown in Fig. 2. The data shown terminates at 5 kbar though on some occasions data were taken to 10 kbar. Noting that the ratio of volume change under pressure (ΔV) to the atmospheric volume (V_0) can be approximated by $3\Delta l/l_0$, $\Delta V/V_0$ was calculated for the glasses by an interpolation process using the data of Vaidya and Kennedy¹⁰, as shown in Table 1, for the alkali halides.

The compressibility of Vaidya and Kennedy was chosen because their measurement is the most recent direct measurement of the compressibilities of all four alkali halides chosen for calibration. Unfortunately their data was taken in a piston cylinder apparatus to 45 kbar so its accuracy is questionable in the pressure range considered in our experiments. Nevertheless it seems advantageous to use data taken by one set of investigators using a single technique. We have reproduced our measurements on KBr within 2% in two independent runs.

Values of the accumulated change in length for the calibrant were calculated from the data of Vaidya and Kennedy and compared with the measured accumulated change in length of the calibrant, as expressed in mV output from the LVDT, at every 0.25 kbar between 1 and 5 kbar. Figure 3 shows a typical display of calibration data showing the scatter in the alkali halide data points. A linear interpolation formula was fitted to the four points by a least squares technique¹¹). The calibration was then used to convert measured instrument output to the change in length of the sample. The arrow shows the measured data point for $\text{Te}_{15}\text{Ge}_3\text{As}_2$, corresponding to a compressibility of $5.75 \times 10^{-12} \text{ cm}^2/\text{dyne}$ at 3 kbar.

The 2% reproducibility of the KBr data together with the internal consistency of a given run would indicate an accuracy of near 2% for the chalcogenide data. However, the inconsistencies within the alkali halides force the assignment of an overall accuracy of only 5%. The calculated values of $\Delta V/V_o$ for the amorphous chalcogenides were fitted to a quadratic equation by a least squares technique. The accuracy of the data did not warrant fitting to a third order or higher equation. The data for the glasses is in Table 2.

The isothermal compressibilities were then calculated from the expression

$$\kappa_T = -\frac{1}{V} \left[\frac{\partial V}{\partial P} \right]_T = -\frac{1}{(1 + \Delta V/V_o)} \left[\frac{\partial}{\partial P} \left(\frac{\Delta V}{V_o} \right) \right]_T$$

since $V = V_o + \Delta V$. The results are also shown in Table 2. The error in the compressibility is about 5%. The present data are some 3% lower than the adiabatic compressibility quoted by Chernov, Dembovskii and Chistov¹²⁾ for As_2Se_3 . The numbers which are calculated both for $\Delta V/V_o$ and for κ_T are very sensitive to the fitting equation chosen. A third order fit would change the extrapolated atmospheric pressure compressibility by about 2%. The coefficient of P in the compressibility is only accurate enough to indicate the direction of the compressibility change with pressure. The compressibilities are shown as changing linearly with pressure because of the quadratic fit chosen for $\Delta V/V_o$. The fact that the compressibilities are decreasing with pressure might be compared with such glasses as SiO_2 whose compressibilities increase with pressure in this pressure range^{3,13)}. It is only at higher pressure that the compressibility of SiO_2 starts to decrease with pressure. The work of Weir and Shartis¹⁴⁾ on the compressibilities of alkali borate and silicate glasses demonstrates that for many glasses the compressibility does indeed decrease with pressure. For the chalcogenide glasses considered here, their compressibilities are 2-3 times greater than those of the silicate glasses and about the same as those of the borate glasses¹⁴⁾.

There was no permanent densification observed within 0.04% in the chalcogenide glasses to 9 kbar when the samples were returned to atmospheric pressure. The atmospheric-pressure adiabatic compressibility¹⁵⁾ of $Te_{15}Ge_3As_2$ leads to a value of the ratio of κ_T/κ_S of 1.08, which is also the heat capacity ratio C_p/C_v . Table 3 gives some values for a variety of other substances for comparison purposes¹⁶⁾. Though the 5% error in κ_T causes the last digit shown for the semiconducting glass to be suspect, there is no apparent trend which

sets this material apart from the others insofar as the compressibility is concerned. The fact that the measured K_T is 3% less than the quoted K_S for As_2Se_3 is indicative of the lack of accuracy in the measurement.

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TABLE 1.

$\Delta V/V_0$ for alkali halides due to Vaidya and Kennedy.
 Pressure (P) in kbar.

	$\Delta V/V_0 \times 10^3$
NaCl	- 4.275 P + .0466 P ²
KCl	- 5.4906 P + .0580 P ²
KBr	- 6.0351 P + .0536 P ²
KI	- 7.886 P + .1129 P ²

TABLE 2.

Measured values of $\Delta V/V_0$ and κ_T for amorphous glasses at 23°C

	$\Delta V/V_0 \times 10^3$ P in kbar	$\kappa_T \text{ cm}^2/\text{dyne}$ P in dynes/cm ²
$\text{Te}_{15}\text{Ge}_3\text{As}_2$	$-(6.23 \pm .3)P + (0.1 \pm 0.05)P^2$	$(6.23 \pm 0.3) \times 10^{-12} - (1.6 \pm 1.0)P \times 10^{-22}$
$\text{Te}_{15}\text{Ge}_2\text{As}_3$	$-(5.86 \pm .3)P + (0.04 \pm 0.05)P^2$	$(5.86 \pm 0.3) \times 10^{-12} - (0.5 \pm 1.0)P \times 10^{-22}$
As_2Se_3	$-(6.43 \pm .3)P + (0.07 \pm 0.05)P^2$	$(6.43 \pm 0.3) \times 10^{-12} - (1.0 \pm 1.0)P \times 10^{-22}$

TABLE 3.

κ_T/κ_S for a variety of materials

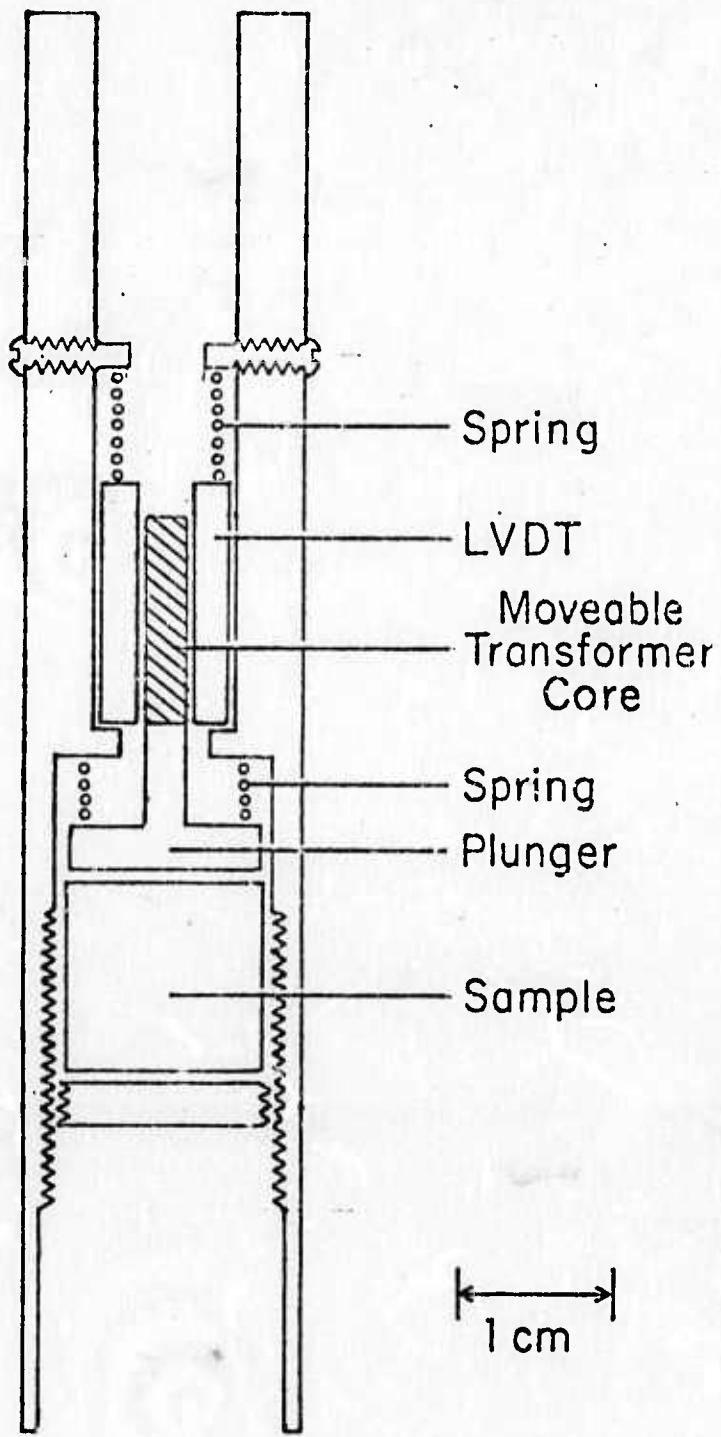
$\text{Te}_{15}\text{Ge}_3\text{As}_2$	1.08	Semiconducting glass
Ge	1.04	Semiconducting crystal
Si	1.01	Semiconducting crystal
SiO_2	1.001	Insulating glass
KCl	1.05	Ionic crystal
K	1.08	Metallic crystal

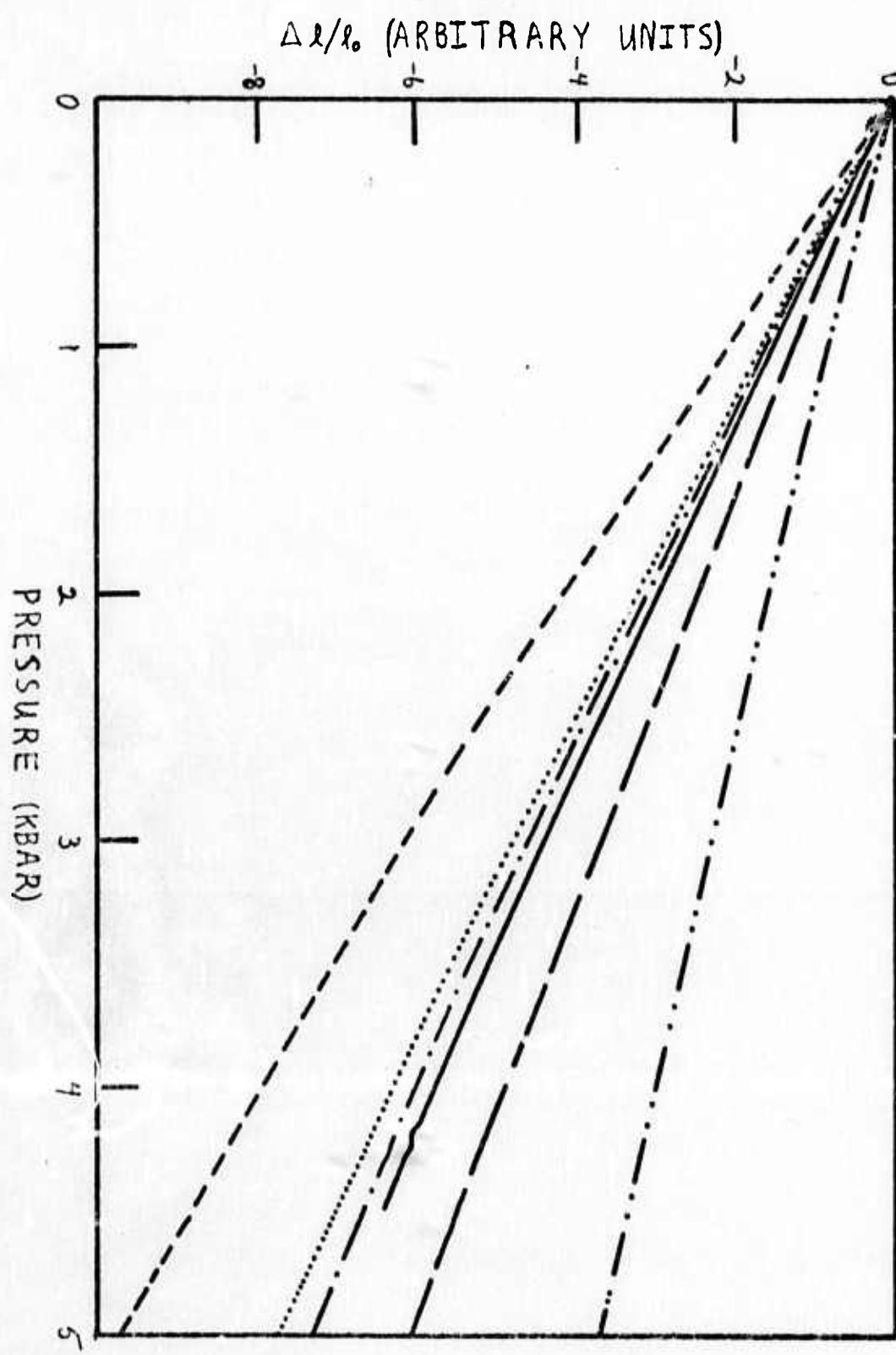
Figure Captions

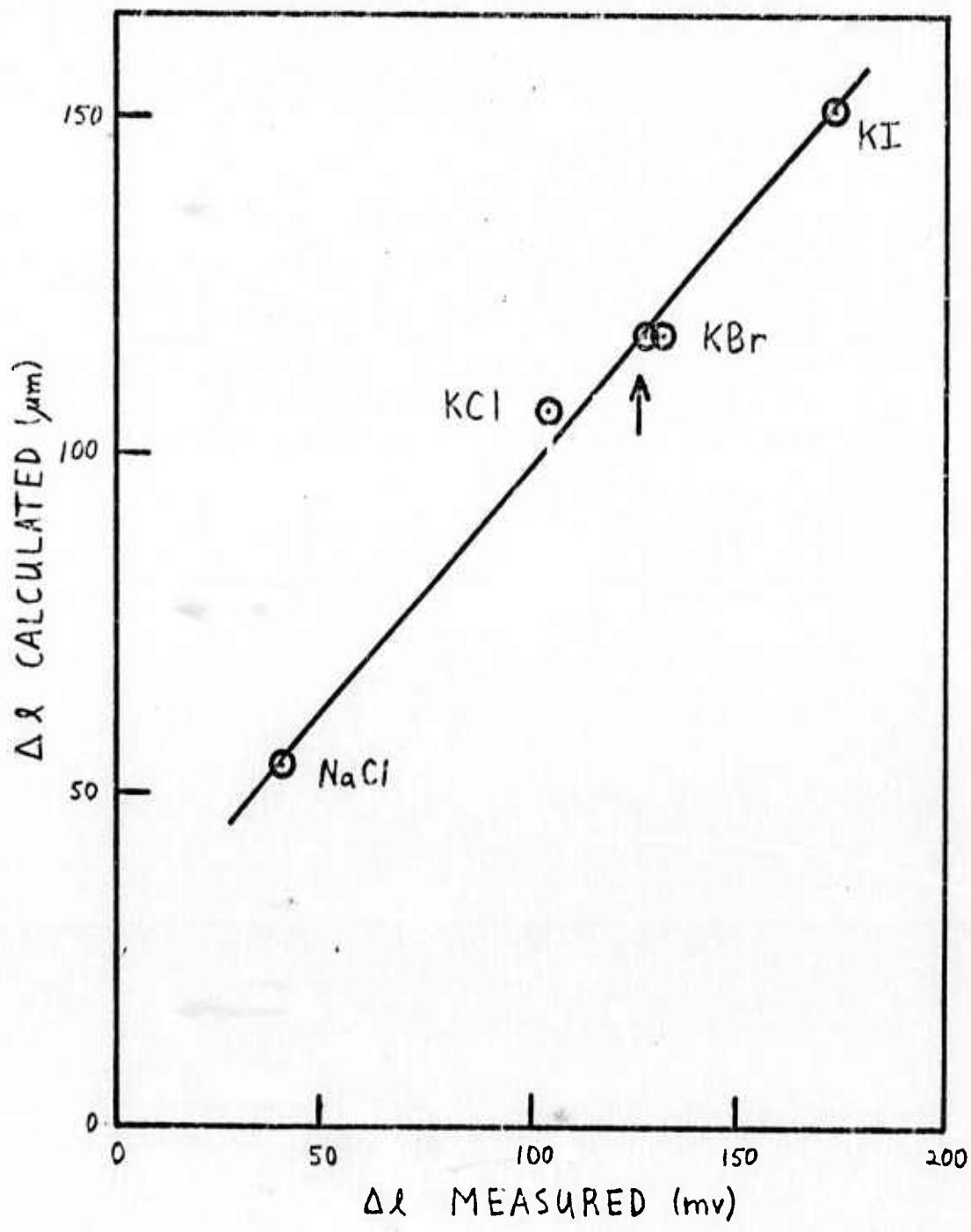
Fig. 1. Cross sectional view of LVDT and sample holder.

Fig. 2. Experimental data on change of length under hydrostatic pressure.
(-·-·-: NaCl; - - - : KCl; —: $\text{Te}_{15}\text{Ge}_3\text{As}_2$; - · - : KBr; · · · : As_2Se_3 ; ---: KI)

Fig. 3. Calibration points at 3 kbar; the arrow marks the measured change
in length for $\text{Te}_{15}\text{Ge}_3\text{As}_2$.







Apparatus for Acoustic Observation of the Glass Transition*

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Abstract

The temperature derivatives of the density and compressibility are known to change when a material undergoes a glass transition. We have developed a procedure whereby the consequent change in reflection coefficient of a 10 MHz acoustic wave at a quartz-sample interface may be used to locate the glass transition. The glass transition detected by high frequency sound is generally at a higher temperature than the transition detected volumetrically. The procedure has been tried out on several organic and chalcogenide glasses.

*Supported by ARPA-monitored by ARO(D); grant No. DA-ARO(D)-31-124-72-G81.

†Robert A. Welch Foundation Undergraduate Scholar.

The glass transition temperature, T_g , is generally observed by changes in a wide variety of properties: viscosity, thermal expansion coefficient, heat capacity (DTA),⁵ compressibility,⁶ dielectric properties,⁷ Mossbauer line width,⁸ NMR⁹ and sound speed.⁶ The procedures near the end of the list tend to give a higher T_g than the others because of the well-known restriction² that T_g varies according to the duration of the experiment—and the duration is essentially the period of the high frequency signal used, say, in dielectric constant or acoustic experiments in contrast to DTA measurements which require several minutes. However, there are indications of the "dc" transition even in megaHertz acoustic measurements as close inspection of the data of Litovitz and coworkers⁶ will reveal. Furthermore, the higher T_g obtained in short duration experiments shifts with composition, pressure, etc., parallel with the conventional, low-frequency transition temperature.¹⁰ It therefore seems possible to use the high-frequency techniques for the determination of T_g as reliably as any other.

We describe here a technique for the determination of T_g using an acoustic signal but avoiding any measure of the sound speed. Instead, the reflection coefficient R , at a quartz-sample interface, is observed.¹¹

The sound speed, c , for an isotropic, fluid medium is given by

$$c = \sqrt{1/\rho K_s} , \quad (1)$$

while the acoustic impedance, Z , is

$$Z = \sqrt{\rho / K_s} , \quad (2)$$

where ρ is the density and K_s the adiabatic compressibility. Changes in density and compressibility at T_g cause the changes in c reported by Litovitz.⁶ Clearly, changes must also occur in Z . Sound speed measurements¹² require knowledge of the sample dimensions, sample size sufficient for a measurable delay, as well as flat parallel ends so that precise measurements in the neighborhood of a phase change are often difficult. Relative impedance measurements, on the other hand, require only one flat face, and a significantly smaller sample.

The amplitude reflection coefficient R is given by

$$R = (Z_1 - Z_2)/(Z_1 + Z_2), \quad (3)$$

where Z_1 is the impedance of the material in which the signal is transmitted and Z_2 the impedance of the sample from which the signal is reflected.

Since Z_1 and any bonding effects are all chosen to be smooth, slow functions of temperature any variation in R must be due to changes in the sample at T_g .

In a glass there are, of course, contributions to C and Z from the shear modulus¹² but the essential observability of T_g remains.

Figure 1 shows a sketch of the apparatus. The sample, at A, is an irregular chip (when solid) polished only at the face which is sealed to the quartz or Al delay line C by some bonding material (e.g., silicone oil) at B. With those glasses for which the liquid state is easily accessible, such as glycerol, a tube is sealed on top of the quartz and the sample poured in. No bond at B is required and a slight tilt of the whole apparatus prevents reflections at the upper surface of the liquid from interfering with reflections at B. The transducer E is sealed onto the quartz at D. The signal at 10 MHz is generated by an Ahrenberg pulsed oscillator. The compressional wave is generated at E, traverses the quartz rod, is reflected at the quartz-sample interface and returns to the transducer for detection. The demodulated reflected pulse is peak detected and the resultant voltage applied to one side of an x-y recorder and a thermocouple to the other. The entire sample-quartz assembly is mounted in a thermocstat appropriate for the substances to be studied.

Initial tests have been directed to those glasses for which previous acoustic data have been published:⁶ pentachlorinated-biphenyl (PCB)¹³ and glycerol. Figure 2 shows data at 10 MHz for PCB. The upper dashed curve is the expected reflectance computed from Ref. 5; though the units of the ordinate are indicated to be arbitrary the deviation from percent reflectance is small. The solid curve is our data as traced from a chart; the arrow near -40°C marks the conventional, dc glass transition. We believe the agreement is quite satisfactory. Even the small break in slope near -40°C is reproduced. The dot-dash curve is the derivative of the data, taken graphically. There is a shift in slope at the dc T_g , a shoulder near -10°C and a peak near +20°C. The peak is to be associated with the glass transition characteristic of the 10 MHz frequency.

The third figure shows similar data for glycerol taken at 10 and 30 MHz. As expected⁶ T_g (ac) shifts to higher temperatures as the frequency increases; the shoulder does not and we do not know its origin at present.

Our interest in this technique lies not in glasses such as these but in amorphous semiconductors. Also, we are more interested in T_g at high pressures (< 10 kb) than at room pressure.¹⁴ We have data on As-Te-Ge glasses and on As_2Se_3 and effects similar to those displayed are observed, as may be seen in Fig. 4. We corroborate conventionally measured T_g 's at atmospheric pressure. Some additional structure between T_g (dc) and T_g (ac) is produced by relaxation of the quartz-sample bond when the sample softens appreciably. Crystallization is also occasionally observed (with an associated decrease in reflectance in our case).

In summary, we believe that we have a relatively simple procedure for detecting T_g which does not require sophisticated equipment or large well-shaped samples and which permits measurements to be made in crowded, hostile environments such as high pressures. This procedure also offers an opportunity to study structural relaxation processes through the frequency dependence of the glass transition temperature.¹⁵

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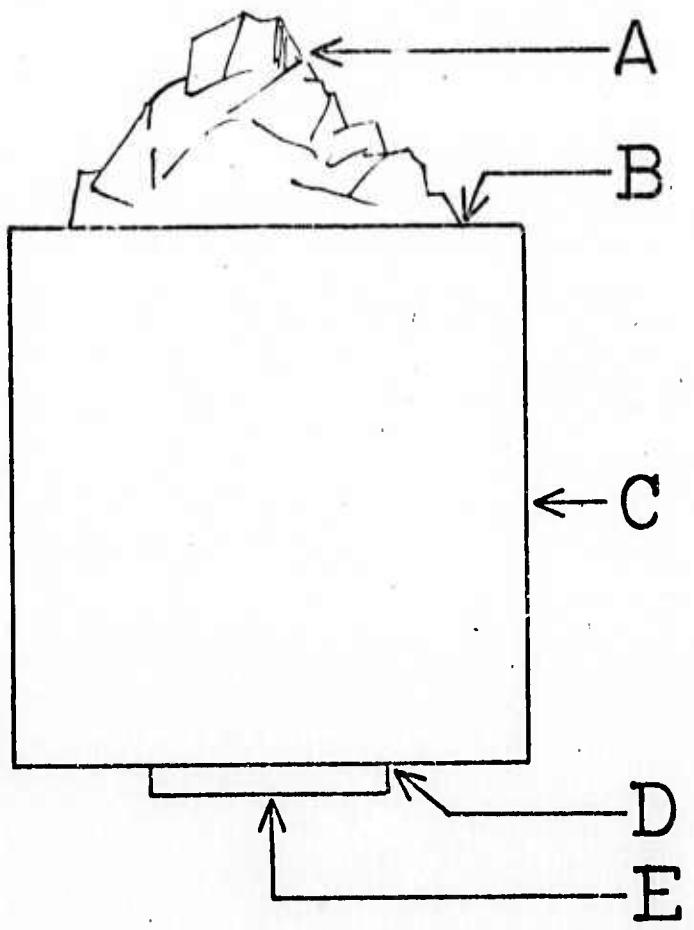
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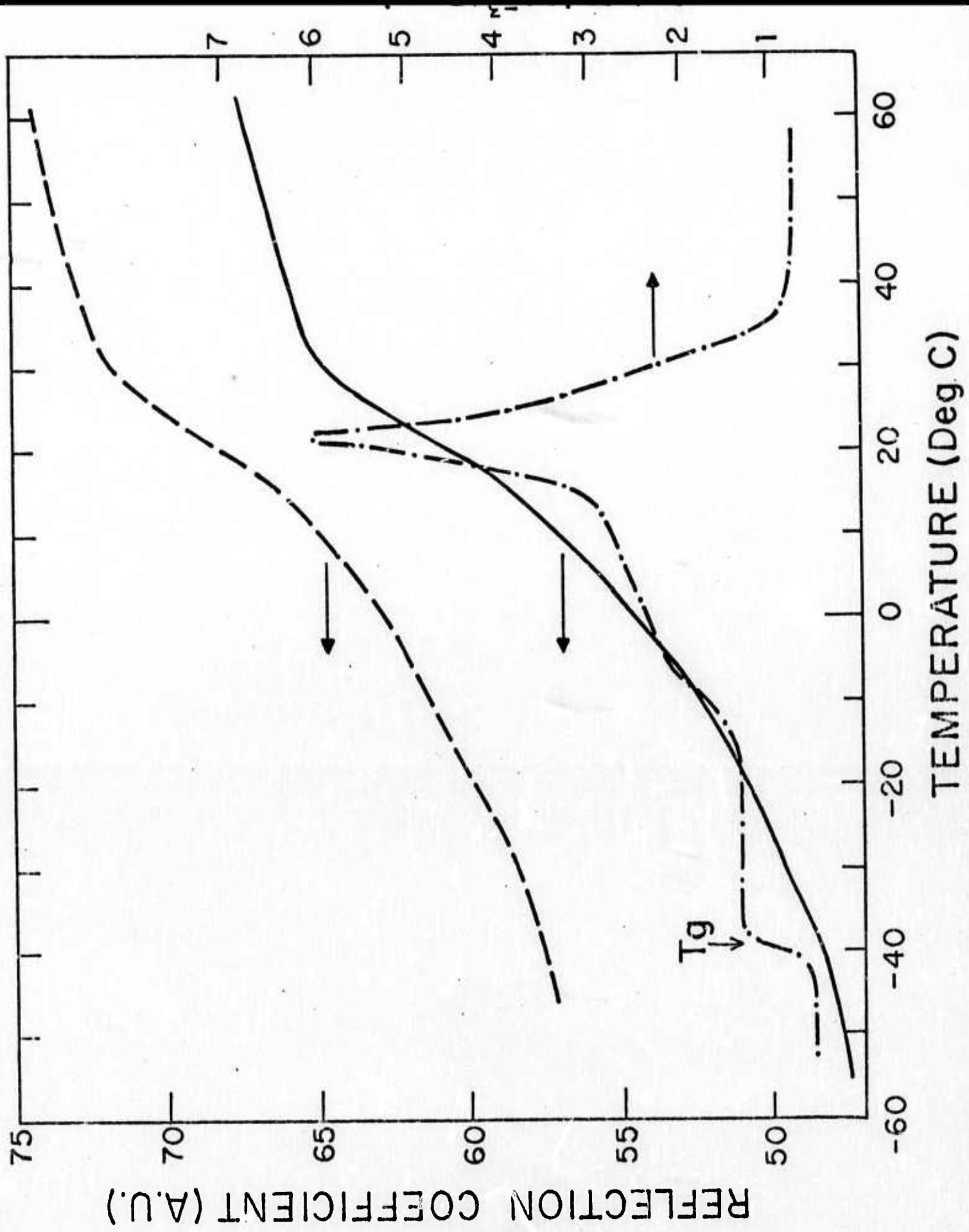
Fig. 1. Schematic representation of apparatus.

Fig. 2. 10 MHz acoustic transition data for PCB. Horizontal arrows point to appropriate scale. Upper dashed curve: calculated reflectance (Ref. 5); solid curve: current work; dash-dot curve: derivative of current work.

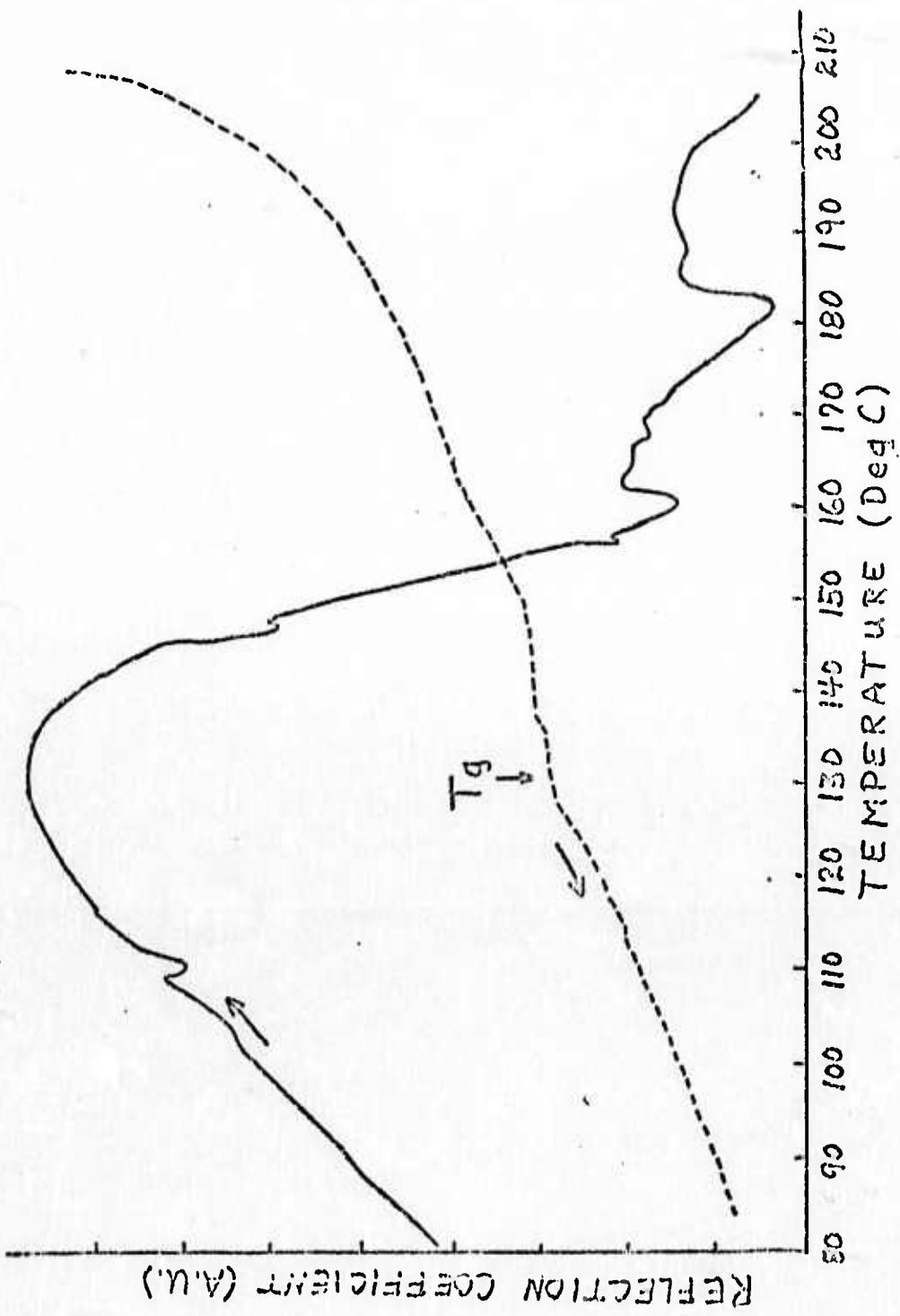
Fig. 3. 10 and 30 MHz acoustic transitions for glycerol. Horizontal arrows point to appropriate scale. Solid curve: 10 MHz signal; dotted curve: 30 MHz signal; dash-dot curve: 10 MHz derivative; dash-dot-dot curve: 30 MHz derivative.

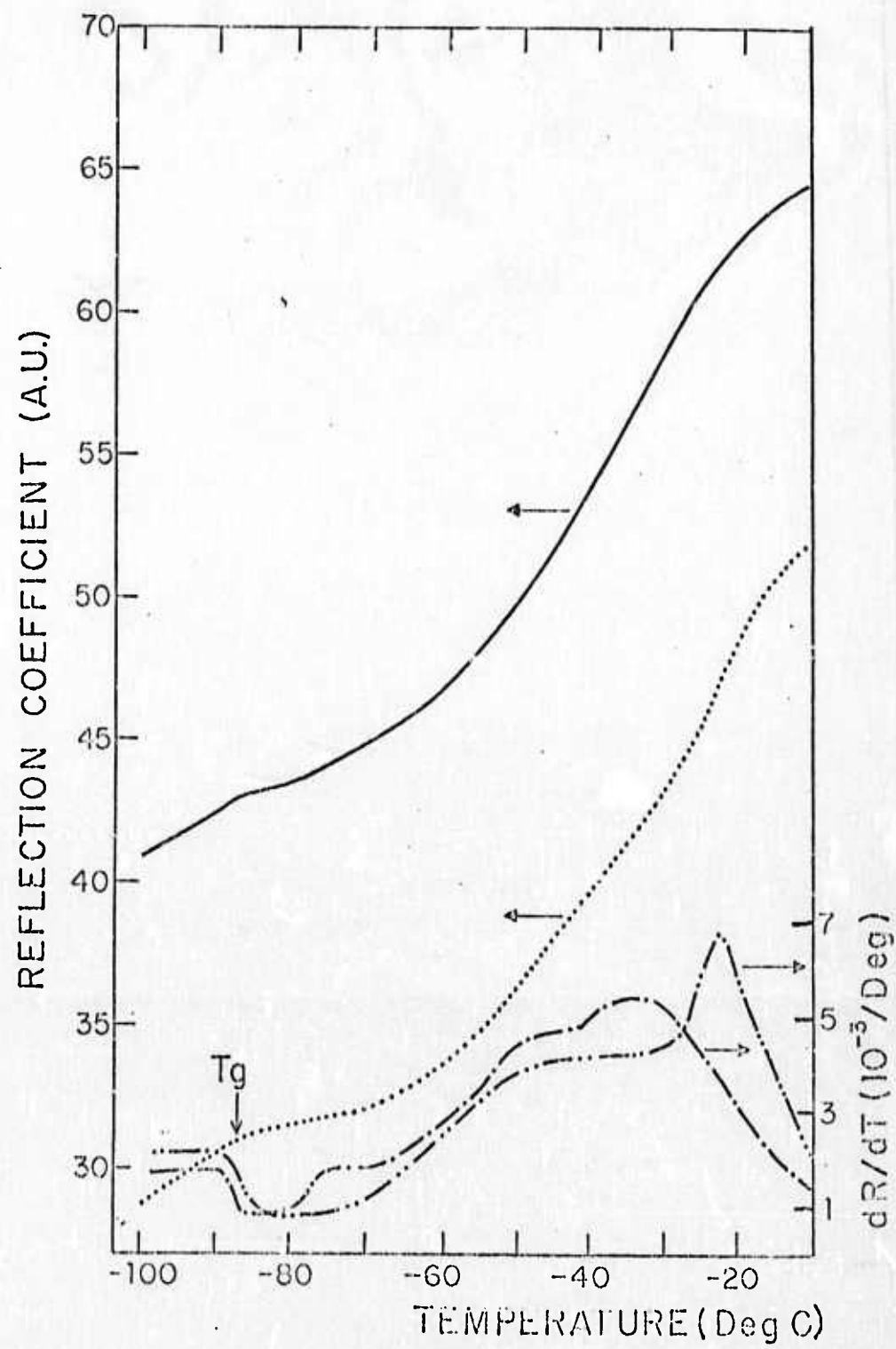
Fig. 4. Acoustic reflection coefficient for $\text{Te}_{75}\text{Ge}_{15}\text{As}_{10}$ at 10 MHz. The heating and cooling curves have been off-set for clarity. Only the cooling curve is used. The dc glass transition is at 130°C and the ac transition near 200°C . The decrease in reflectivity observed on heating above 140°C is due to improved bonding of sample and delay line on first softening of the sample. Subsequent cycles with the same sample do not show hysteresis.





REFLECTION COEFFICIENT (A.U.)





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